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A STUDY OF THE DETERMINATION OF BROMIDES  
IN THE PRESENCE OF EXCESS CHLORIDES

BY

MAYOR FARTHING FOGLER  
B.S. University of Illinois, 1920

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1921



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UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

August 1, 1921.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Mayor Farthing Fogler  
ENTITLED A Study of the Determination of Bromides in  
the Presence of Excess Chlorides  
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
THE DEGREE OF Master of Science.

J. H. Reedy,

In Charge of Thesis

Geo. H. Keel

Head of Department

Recommendation concurred in\*

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\_\_\_\_\_

Committee

on

Final Examination\*

\*Required for doctor's degree but not for master's



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A Study of the Determination of Bromides  
in the Presence of Excess  
of Chlorides.

I. Introduction.

A fundamental problem in the bromine industry is the accurate estimation of the bromide content of the brines or bitters. Since the bromide content is low -- usually less than 5% -- this problem involves the determination of bromides in the presence of a large excess of chlorides. It is important because it is desirable to know just how much bromine is present, so as to add exactly the equivalent amount of oxidizing agent needed to effect its liberation. Various methods in current use which give satisfactory results for high concentrations give very divergent results for low concentrations. The purpose of this investigation is to study the methods for estimating bromine and to ascertain, if possible, the cause of their inaccuracy.

II. Historical.

Chemical literature contains numerous methods that have been proposed for this analysis, most of them depending on





a selective oxidation of the bromide and its subsequent titration or gravimetric determination. Vortman<sup>1</sup> who attempted to determine chlorine in the presence of bromine used lead dioxide in the presence of acetic acid to oxidize the bromides and then determined gravimetrically the chlorine which remained in the solution. The results were always high because the bromine was not all set free, while if a higher concentration of acetic acid was used traces of chlorine were liberated. Cavazzi<sup>2</sup> used barium peroxide and sulfuric acid as the oxidizing agent. The bromine was distilled, but a little chlorine was also liberated. Engle<sup>3</sup> tried to use ammonium persulfate and sodium acetate at 70° -80°. Berglund<sup>4</sup> used potassium hydrogen sulfate and potassium permanganate in the cold, and aspirated air through the solution to remove the bromine, collecting it in sodium hydroxide solution. He reports that the bromine was then determined gravimetrically, though no statement is made as to how the sodium hypobromite formed was reduced. It was found, moreover, that while the oxidizing agent would not liberate chlorine if it alone were present, it did liberate chlorine when bromine was present. He avoided this by a double aspiration. Baubigny and Rivals<sup>5</sup> used copper sulfate and potassium permanganate at the constant temperature of 20°, but with little success, as chlorine was also liberated. Wyss<sup>6</sup> attempted to separate all of the halogens by selective oxidation. He first removed the iodine by ferric sulfate, and then added





potassium permanganate and heated to 60° to liberate the bromine which was determined gravimetrically. He stated that his method gave good results, but offered no figures to support his claim. White<sup>7</sup> used aluminium sulfate and potassium permanganate and stated that bromine was liberated while chlorine and iodine were not. It is quite inconceivable how an oxidizing agent could have sufficient oxidizing power to liberate bromine and at the same time not liberate iodine which is much more readily oxidized. Jannasch and Aschoff<sup>8</sup> used acetic acid and permanganate to liberate the bromine but their results were always low. Bugarszky<sup>9</sup> very carefully investigated other methods proposed, and himself used iodic acid to free bromine, but obtained very poor results. Andrews<sup>10</sup> used iodic acid to oxidize the bromide and found it very suitable if the bromine was present in large quantities. But this method is hardly applicable where chlorine is present in large quantities. Later investigators have found out that the oxidation potential of the oxidizing agent must lie between that of bromine and chlorine. As an oxidizing agent of the correct potential iodic acid has been used, as mentioned above. Gooch<sup>11</sup> used selenic and telluric acids, but neither works well unless chlorine is present in very minute amounts. Skinner and Baughman<sup>12</sup> used hydrogen peroxide and chromic acid to liberate the bromine, which was removed by aspiration in the cold. They found that chlorine also came over from a saturated solution to the extent of



about 1%. This was remedied by double aspiration. They obtained very good results, but the method is rather long and involved.

None of the above methods are adapted to rapid, accurate work, and some of them admit of errors as large as 2%. Those that are fairly accurate require several hours or even days for their completion. It would appear, then, that the optimum method has not yet been developed.

### III. Experimental.

There are in general two methods for determining bromides in the presence of an excess of chlorides: (1) The gravimetric method, which involves the precipitation of the bromine and all or part of the chlorine as silver halides and the subsequent estimation of the composition of the precipitate, either by indirect analysis or calculation; (2) The selective oxidation of the bromine, using an oxidizing-agent that will not liberate chlorine, or at least only a small amount.

#### A. Gravimetric Methods.

Precipitation of Silver Bromide in the Presence of Excess of Chlorides--A gravimetric method that appears -- on its face, at least -- to be both rapid and accurate, involves the addition of a known amount of silver nitrate to the halide solution in a quantity somewhat in excess of that needed to completely precipitate the bromine. The amount of bro-





mine present may be calculated from the following expression:

$$\begin{aligned} \text{Wt. of Br} &= 1.7976 \times \text{Wt. of AgBr} + \text{AgCl} - \\ &\quad 2.3885 \times \text{Wt. of Ag.} \end{aligned}$$

The excess of silver nitrate over the amount necessary to preceipitate the bromine should be small. This follows from the fact that, for mixtures of silver bromide and silver chloride,

$$\% \text{ AgBr} = 100 - \frac{100 \times \text{Wt. of AgCl}}{\text{Wt. of AgBr} + \text{AgCl}}.$$

Now, in case of an error in the weight of the silver halide precipitate, the effect on the result will be small if the amount of silver chloride is small; but if the latter is large, the value of the fraction in the above expression will be increased considerably; that is, the magnitude of the inaccuracy will be multiplied as many fold as the weight of the silver chloride is increased.

The accuracy of this method depends on the assumption that the bromine is quantitatively precipitated by the silver nitrate before appreciable amounts of silver chloride are formed. This inference is justified by a comparison of the solubility products of the two halides.

Precipitation from Ammonium Hydroxide Solutions--It was felt that the above method was open to criticism in that, owing to the speed of the reaction, the silver nitrate might be used up locally in the formation of silver chloride, leaving unprecipitated bromides in the solution. It is known



that the conversion of silver chloride into silver bromide by means of soluble bromides is low. Hence if the precipitation could be made to proceed slowly, the silver bromide precipitation would occur first, and the silver chloride precipitation would not begin until the former is complete. In order to do this it is necessary to use a solvent for the silver halides that may be gradually removed, or else to add the silver nitrate very slowly. Ammonium hydroxide was the first solvent to be used. The experiments were carried out as follows: Solutions of potassium bromide and potassium chloride were mixed, a volume of ammonium hydroxide added, and then enough silver nitrate to precipitate all the bromine and part of the chlorine. The beaker containing the mixture was heated to boiling and stirred vigorously until all the ammonia was driven out. Any traces were neutralized by the addition of dilute nitric acid, and the precipitate filtered in a Gooch crucible, dried and weighed. Table I shows typical results.

Table I. Results with Ammonium Hydroxide as Solvent.

Exp.	Per cent KCl	Amount of AgBr Theory	Amount of AgBr Found	Difference
1	2%	1.5480 gm.	1.5254 gm.	-.0126 gm.
2	2%	1.5480	1.4850	-.0630
3	2%	1.5480	1.5405	-.0075
4	2%	1.5480	1.4945	-.0535
5	2%	1.5480	1.4861	-.0619
6	2%	1.5480	1.5333	-.0147
7	2%	1.5480	1.4666	-.0814
8	2%	1.5480	1.4260	-.1220
9	2%	1.5480	1.4789	-.0691
10	2%	1.5480	1.4996	-.0484
11	2%	1.5480	1.4771	-.0709





It will be noted that the results were always low, indicating incomplete precipitation of either the bromine or the silver. This fact will be interpreted later.

Alcohol as a Solvent--It was thought that the silver halides were both too soluble in ammonium hydroxide to get consistent results, so some other solvent was sought for. It was observed that silver chloride is appreciably soluble in ethyl alcohol, while silver bromide is not. So the above determinations were repeated, except 50% alcohol was used as the solvent. Table II shows the results.

Table II. Results with 50% Alcohol as Solvent.

Exp.	Per cent KCl	Amount of AgBr Theory	Amount of AgBr Found	Difference
1	2%	1.5480 gm.	1.5518 gm.	+.0038
2	2%	1.5480	1.5158	-.0312
3	2%	1.5480	1.4956	-.0524
4	2%	1.5480	1.5231	-.0249
5	2%	1.5480	1.5080	-.0400
6	2%	1.5480	1.5100	-.0380
7	2%	1.5480	1.5268	-.0212
8	2%	1.5480	1.5328	-.0152
9	2%	1.5480	1.5121	-.0359
10	2%	1.5480	1.5334	-.0146

Water as a Solvent--Mainly for the purpose of comparison with the above results, a series of determinations was made with water as the solvent. Table III shows the results.

Table III. Results with Water as Solvent.

Exp.	Per cent KCl	Amount of AgBr Theory	Amount of AgBr Found	Difference
1	2%	1.5480	1.5228	-.0252
2	2%	1.5480	1.5250	-.0230
3	2%	1.5480	1.5344	-.0126
4	2%	1.5480	1.5098	-.0382



The results in the experiments in water solution are distinctly better than with ammonium hydroxide and alcohol as solvents, but still they fall far below the usual standard for accuracy.

To meet the suggestion that the low results were due to the bromine not being completely precipitated, owing to the slow conversion of silver chloride into silver bromide, the following experiment was made: The silver in 4 cc. of normal silver nitrate was completely precipitated as silver chloride and then stirred with an excess of sodium bromide solution for six hours, after which it was found that about 75% of the chlorine had been replaced by bromine. In the precipitation of silver from silver nitrate solution by mixed halides, on the other hand, the silver halide is formed in a very highly dispersed condition, which has a far higher solubility than the coagulated form, and in this state the bromine seems to replace the chlorine in a comparatively short time. It would appear that the magnitude of these dispersed particles is so small that no particle is large enough to permit of the formation of a protective coating of silver bromide and thus prevent the inner part from reacting with the sodium bromide.

Cause of Low Results--The cause of the low results in the precipitation methods is to be found in the solvent action of alkaline halides on silver bromide and silver chloride. Schierholz<sup>13</sup> has reported that 100 grams of sodium chloride in concentrated solution dissolve 0.474 grams of silver bro-





mide, and 100 grams of potassium bromide in concentrated solution dissolve 3.019 grams of this salt, the temperature being 15° in both cases. In a similar way, silver chloride is also dissolved by solutions of concentrated alkaline halides.

Empirical Corrections for Low Results--The expedient of deriving a set of solubility values for silver bromide in alkaline halides was then taken up. Given these data, empirical corrections could be made on all analytical results. So it was planned to construct a solubility curve for silver bromide in concentrations of sodium chloride varying from 1% to saturation. The determinations were made as follows: 50 cc. of approximately 0.1 N silver nitrate were taken and just enough sodium bromide was added to precipitate all of the silver as silver bromide. Results are given in Table IV.

Table IV. Solubility of Silver Bromide in Sodium Chloride Solution.

Grams per 100 cc. of Solution	Weight of AgBr Theory	Weight of AgBr Found	Weight of AgBr Dissolved
1	.9354	.9178	.0176
1	.9354	.9100	.0254
1	.9354	.9169	.0185
1	.9324	.9204	.0120
1	.9324	.9193	.0131
1	.9324	.9200	.0124
1	.9798	.9706	.0092
1	.9798	.9705	.0093
1	.9798	.9712	.0086
2	.9354	.9087	.0267
2	.9354	.9044	.0310
2	.9354	.9087	.0267



Table IV--Cont.

Grams per 100 cc. of Solution	Weight of AgBr Theory	Weight of AgBr Found	Weight of AgBr Dissolved
2	.9324	.9133	.0191
2	.9324	.9195	.0129
2	.9324	.9143	.0181
2	.9798	.9668	.0130
2	.9798	.9683	.0115
2	.9798	.9656	.0142
3	.9354	.9012	.0342
3	.9354	.9025	.0329
3	.9354	.9027	.0327
3	.9324	.9082	.0242
3	.9324	.9100	.0226
3	.9324	.9077	.0247
4	.9354	.8986	.0368
4	.9354	.8959	.0395
4	.9354	.8976	.0378
4	.9324	.9055	.0269
4	.9324	.9060	.0264
4	.9798	.9605	.0293
4	.9798	.9597	.0301
4	.9798	.9582	.0316
5	.9354	.8900	.0454
5	.9354	.8908	.0446
5	.9354	.8905	.0449
5	.9324	.9014	.0310
5	.9324	.9022	.0302
6	.9354	.8905	.0449
6	.9354	.8902	.0446
6	.9354	.8900	.0448
6	.9324	.9000	.0324
6	.9324	.8994	.0330
7	.9354	.8871	.0483
7	.9354	.8885	.0469
7	.9324	.8958	.0368
7	.9324	.8958	.0368
7	.9324	.8952	.0374





Table IV--Cont.

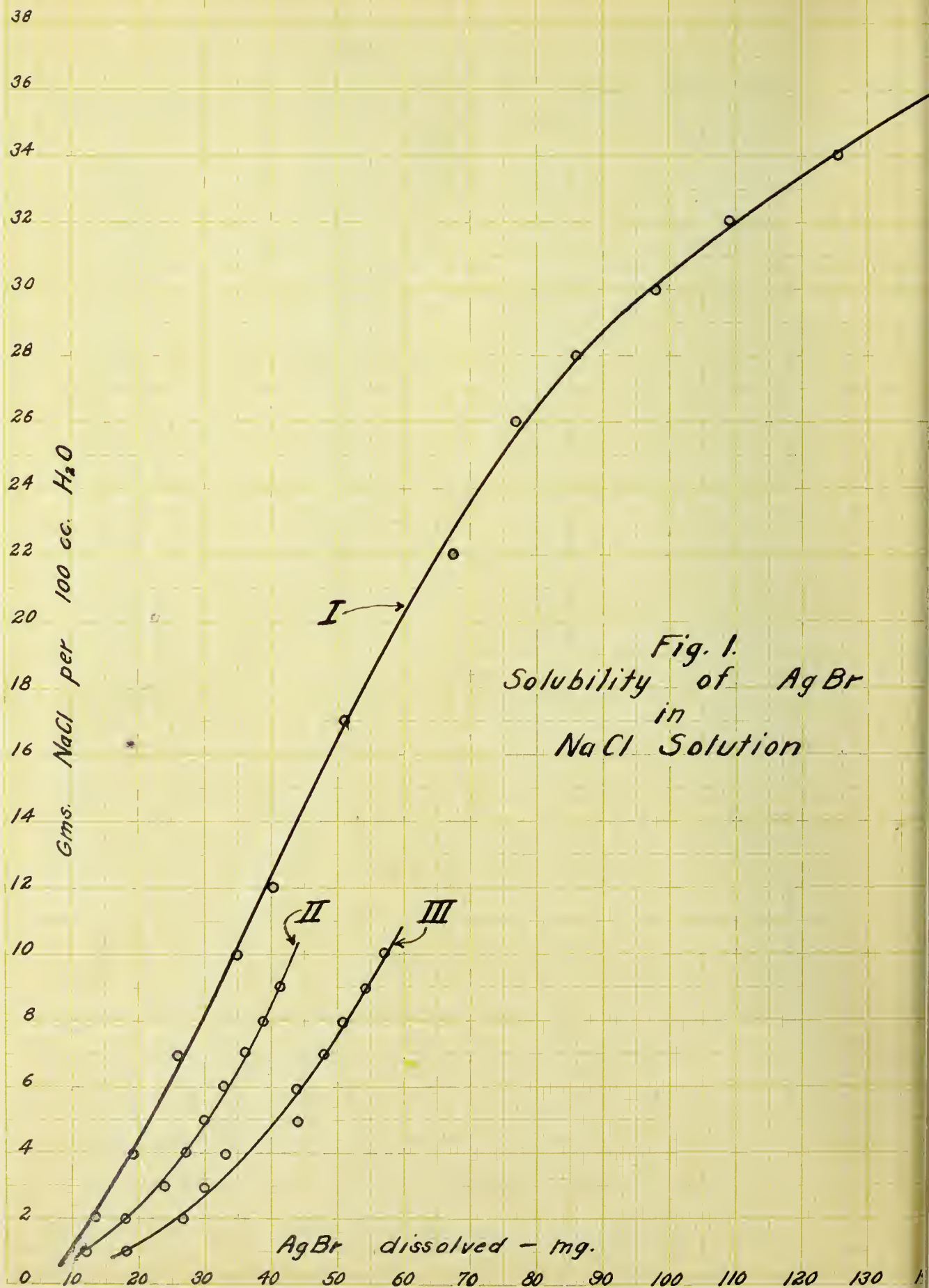
Grams per 100 cc. of Solution	Weight of AgBr Theory	Weight of AgBr Found	Weight of AgBr Dissolved
7	.9798	.9537	.0267
7	.9798	.9520	.0278
7	.9798	.9526	.0272
8	.9354	.8830	.0511
8	.9354	.8836	.0505
8	.9324	.8945	.0379
8	.9324	.8945	.0379
8	.9324	.8939	.0385
9	.9354	.8822	.0532
9	.9354	.8815	.0539
9	.9354	.8817	.0537
9	.9798	.9473	.0325
9	.9798	.9507	.0291
9	.9798	.9458	.0340
10	.9354	.8771	.0581
10	.9354	.8790	.0562
10	.9354	.8784	.0568
10	.9758	.9444	.0354
10	.9758	.9444	.0354
10	.9758	.9440	.0358
11	.9798	.9400	.0398
11	.9798	.9416	.0382
11	.9798	.9389	.0409
12	.9798	.9396	.0402
12	.9798	.9389	.0409
17	.9798	.9228	.0570
17	.9798	.9282	.0516
17	.9798	.9290	.0508
20	.9798	.9185	.0613
20	.9798	.9184	.0614
20	.9798	.9141	.0657
22	.9798	.9140	.0658
22	.9798	.9127	.0671
22	.9798	.9129	.0669



Table IV--Cont.

Grams per 100 cc. of Solution	Weight of AgBr Theory	Weight of AgBr Found	Weight of AgBr Dissolved
24	.9798	.9079	.0719
24	.9798	.9127	.0671
24	.9798	.9120	.0678
26	.9798	.9042	.0756
26	.9798	.9040	.0758
26	.9798	.9082	.0716
28	.9798	.8924	.0874
28	.9798	.8909	.0887
28	.9798	.8937	.0861
30	.9798	.8830	.0968
30	.9798	.8805	.0993
30	.9798	.8797	.1001
32	.9798	.8681	.1117
32	.9798	.8699	.1099
34	.9798	.8540	.1258
34	.9798	.8591	.1207
34	.9798	.8538	.1260
36	.9798	.8408	.1390
36	.9798	.8409	.1389
36	.9798	.8450	.1348

In the above table the results from one and the same solution are set off in blocks of three, or sometimes two. It will be noticed that, for the most part, there is good agreement within these blocks. For different blocks, however, where solutions of sodium bromide of different concentrations were used in preparing the silver bromide, and where uniform conditions were not maintained, the results are markedly different. Take, for example, the solubilities in 1% sodium chloride solution. The first three determinations are from the same concentration of sodium bromide, were run at the same time, and under conditions that were iden-





tical, including concentration, heating, stirring, and so forth.

This indefiniteness in the solubility of silver bromide is explained by the fact that substance is a colloid, and the size of the particles depends on such conditions as those just mentioned. And in turn, the solubility of a solid depends on the size of the particles, the solubility increasing enormously with the degree of subdivision.

Attempts were made to regulate the conditions by carrying out all determinations alike. For example, each precipitate was stirred for a definite time to coagulate the particles, and washed with a definite amount of water. In this way better checks were obtained. If a solution of sodium bromide of the same concentration were used throughout, good results could probably be obtained and a fairly smooth solubility curve drawn for the solubility of silver bromide in various strengths of sodium chloride solution. Figure I shows three solubility curves plotted from the data in Table IV. Curve I was plotted from solubility measurements on silver bromide made by mixing .0994 N sodium bromide and .1043 N silver nitrate in equivalent amounts; curve II from .1007 N sodium bromide and .0993 N silver nitrate; curve III from .1006 N sodium bromide and .0996 N silver nitrate. Other conditions than concentration were practically the same in all cases.

It will be seen therefore that the amount of silver bromide which dissolves in a certain concentration of sodium



chloride solution is not constant unless all details of technique are regulated so as to be exactly identical in every case. These, of course, can not be regulated on an unknown sample. Therefore it is not possible to determine bromine in a solution of this kind by precipitating and weighing it and then adding an empirical correction which corresponds to its solubility in that concentration of sodium chloride solution.

#### B. Selective Oxidation Methods.

Methods involving the selective oxidation of bromides to free bromine and the subsequent distillation of the liberated halogen offer certain advantages, the most important of which is the concentration of the bromine. Later work has shown that it is not always possible to make a "clean" separation from chlorine in this way, since varying amounts of the latter are usually present in the distillate. But it does have the advantage of reducing the chloride concentration very considerably. The importance of this point is evident when it is remembered that the halogen content of the distillate is almost always determined gravimetrically, and, as has been shown above, the gravimetric method has the maximum accuracy when the amount of chlorine is a minimum.

The whole range of oxidizing agents has been explored by investigators in their efforts to find one that will preferentially oxidize the bromine without affecting the chlorine. Nitrosyl sulfuric acid ("nitrose"), chromic acid, acidified potassium permanganate, and so forth, have been





used with more or less uncertain success.

An important point in the technique of these distillation methods is that the halogens of the distillate must be absorbed in some suitable reducing agent which will reconvert them into bromides and chlorides, respectively. If silver nitrate were also present in this absorbing medium, the halogens would be immediately precipitated in their final form for weighing. The use of silver nitrate without a reducing agent would lead to low results, owing to the formation of oxidized bromine compounds like hypobromous acid and silver bromate.

Sodium Sulfite as a Reducing Agent--The first agent tried was sodium sulfite. The determination was carried out as follows: 50 cc. of 0.1 N sodium bromide was placed in a distilling flask and an amount of sodium chloride was added and the solution diluted to about 100 cc. To this was added 12 grams of chromic acid and about 2 cc. of 30% hydrogen peroxide, and the mixture distilled. The solution in which the halogens were to be absorbed consisted of 5 cc. of 0.1 N silver nitrate and the calculated amount of sodium sulfite. The distillation was run for about 30 minutes. The precipitate was coagulated by stirring, collected in a Gooch crucible, dried and weighed. Results were as follows:

Br Present	Br Found
1.0562 gm.	.9898 gm.
1.0562	.9853



The results in these determinations were low because the sodium sulfite reduced some of the silver nitrate to free silver on heating. In order to avoid this complication a series of experiments were conducted in which the absorbing solution was not heated. Results were:

Br Present	Br Found
.9865 gm	.9930 gm.
.9865	.9870
.9865	.9948
.9865	.9898

These values are high -- presumably because varying amounts of chlorine were carried over during the distillation.

The next determinations were made by absorbing the bromine in sodium sulfite solution, then acidifying with sulfuric acid and boiling, so as to expell the sulfur dioxide. Silver nitrate solution was then added, and the bromine determined in the usual way. Only a small excess of oxidizing agent was used in the reaction flask beyond what was theoretically required to liberate the bromine, so as not to oxidize the chlorine if possible. Results:

Br Present	Br Found
.9865 gm.	.9822 gm.
.9865	.9843

These determinations show that the oxidation of the bromides was not complete, and that an excess of oxidizing agent is necessary to effect its quantitative expulsion.

Oxidizing Agents--The chromic acid-hydrogen peroxide mixture is not a very satisfactory oxidizing medium, because if the mixture is heated long enough to drive off all





of the bromine large amounts of chromyl chloride distill over, and thus too large an excess of silver nitrate must be used to precipitate all of the halogen present.

Another oxidizing agent experimented with was hydrogen peroxide in the presence of sulfuric acid. It was observed that hydrogen peroxide in the presence of concentrated sulfuric acid will liberate bromine from sodium bromide solution at  $50^{\circ}$  -  $60^{\circ}$ , or even a lower temperature, while the chlorine in sodium chloride solution appears unaffected until the solution is brought to a boil. This would suggest that it might be possible to liberate bromine almost quantitatively from a solution of the halides by this reagent. In order to ascertain if all the bromide could be oxidized quickly and also to find out if it would be completely absorbed in silver nitrate solution to which hydrogen peroxide had been added to act as a reducing agent, a series of experiments was made in which no chlorine at all was present. The reactions involved are as follows:



This is an oxidation reaction, the hydrogen peroxide acting as the oxidizing agent. In the following reaction it conducts itself as a reducing agent:



These experiments were carried out in the following manner: 20 cc. of the sodium bromide solution was placed in an aspirator bottle and 2 cc. of 30% hydrogen peroxide and 5 cc. of concentrated sulfuric acid added. The liberated bromine





was then removed by aspiration and collected in nitrogen bulbs containing 25 cc. of dilute silver nitrate solution and about 2 cc. of 30% hydrogen peroxide. The solution in the aspirator bottle became colorless after aspiration for about one-half hour. The results were as follows:

Br Present	Br Found
.4012 gm.	.4027 gm.
.4012	.4013
.4012	.4018
.4012	.4023

Why these results should be somewhat high has not been accounted for. However, it should be noted that this method gives decidedly the most satisfactory results of all those tried.

The following determinations were made on solutions of sodium bromide in 7% sodium chloride, using only a slight excess of silver nitrate to collect the bromine:

Br Present	Br Found
.4012 gm.	.3656 gm.
.4012	.3683
.4012	.3678

The following were made using a larger excess of silver nitrate:

Br Present	Br Found
.4012 gm.	.4119 gm.
.4012	.4147
.4012	.4110
.4012	.4163

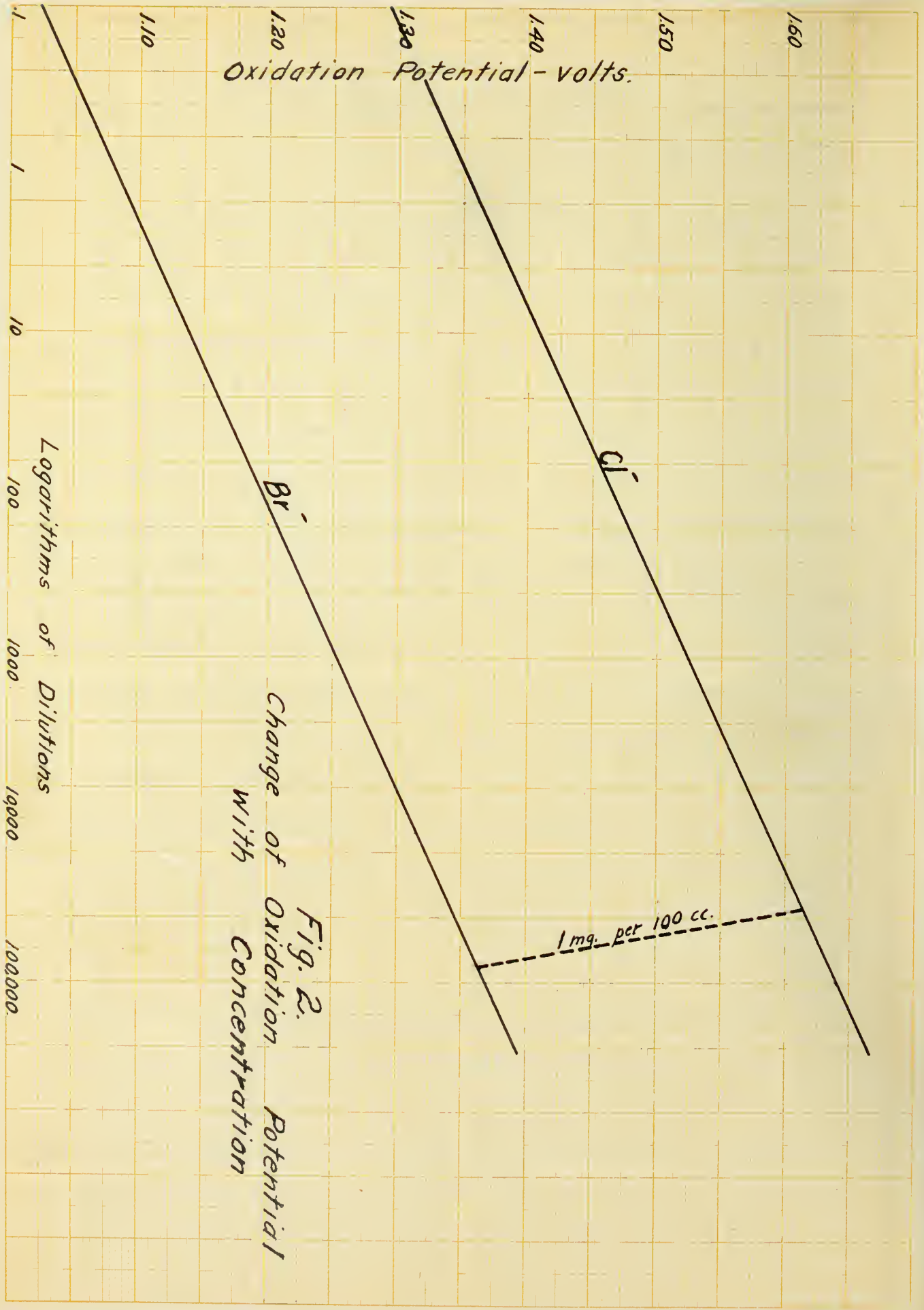
This demonstrates the fact that even in fairly dilute solutions of sodium chloride the sulfuric acid will liberate hydrogen chloride, which may be more or less oxidized to



free chlorine. At any rate the silver precipitate contains silver chloride.

Fixation of Bromine by Metallic Silver--An interesting possibility suggested itself in the expedient of absorbing the bromine by passing the aspirated gases through a tube containing finely divided silver. The principle upon which this conjecture was based is the very general belief that bromine will react with metallic silver while hydrochloric acid will not. The procedure was as follows: Very fine crystals of pure silver were prepared by electrolyzing silver nitrate between a silver anode and a platinum cathode. These were carefully washed and dried, and placed in a tube through which the gases were to be drawn. Upon trial, however, taking no precautions to dry the gases, the increase in weight was too high, indicating that moist hydrochloric acid will react with fine divided silver. Upon introducing between the tube and the flask wash bottles containing concentrated sulfuric acid to dry the gases, the increase in weight was practically nil, showing that silver will not combine with dry bromine.

Theory of Oxidation of Bromides and Chlorides--The fact that no one has found an oxidizing agent that will selectively oxidize the bromine finds a complete explanation in thermodynamic considerations. According to thermodynamics, the chemical work done in these oxidations depends wholly upon the "initial and final states" and is "independent of the





path" -- that is, the oxidizing agent used. By "initial and final states" is meant particularly concentration conditions. This doctrine teaches, therefore, that the expenditure of energy in effecting the oxidation of a certain amount of bromide ions at definite concentration to bromine is a constant, and that a certain "thermodynamic potential" is necessary for the process. As a measure of this thermodynamic potential may be used the electrical potential necessary to bring about electrically the oxidation, which of course is equal to the change in "free energy" involved. It is possible, of course, that a particular oxidizing agent might be somewhat "faster" than another agent, and in this way show selective action. But for similar ions like  $\text{Br}^-$  and  $\text{Cl}^-$ , this is not likely.

Figure II shows the relation between the concentrations of the halogen ions,  $\text{Br}^-$  and  $\text{Cl}^-$ , and the oxidizing potential necessary to convert them into free halogens. These graphs have been calculated by means of the well-known Nernst formula from the values of the normal bromine and chlorine electrodes. The temperature is assumed to be  $25^\circ \text{C}$ . The horizontal axis shows the dilutions (that is, the reciprocals of the concentrations) expressed in terms of their logarithms. Using 0.1 milligram of bromine as the limit of analytical error, the potential necessary to reduce the  $\text{Br}^-$ -ion concentration (using 100 cc. of solution) to that point has been calculated by the figure to be 1.36 volts, referred to the normal hydrogen electrode as 0.0 volts. This potential,





however, as also shown by the figure, is sufficient to oxidize  $\text{Cl}^-$ -ions of concentrations greater than 0.6 N sodium chloride -- that is, a concentration of 3.5% by weight. This shows very decidedly why selective oxidation methods will not bring about a complete separation of bromine from moderate concentrations of sodium chloride like 5% -- which is a weak strength as brines and bitterns go. For higher concentrations, approaching saturated sodium chloride solution, liberation of the chlorine may begin when 100 cc. of the solution still contain as much as 4.5 milligrams of unoxidized bromide.

Method Recommended--The results obtained in this work as discussed above indicate very conclusively that bromine can not be separated quantitatively from an excess of chlorides by selective oxidation and distillation, since oxidation of the chloride begins before the bromine is completely expelled. The best method is the following: The halide mixture is placed in an aspirator bottle and 2 cc. of 30% hydrogen peroxide and about 5 cc. of concentrated sulfuric acid added. The halogens are collected in a known amount of dilute silver nitrate containing a volume of pure hydrogen peroxide -- for example, 2 cc. of the 30% product. After the aspiration has continued for about three quarters of an hour, the vessel containing the absorbing medium is disconnected and placed on a water bath until the solution "brightens." Now dilute potassium chloride solution is carefully added drop by drop as long as a precipitate forms. The pre-



cipitate is then treated in the usual way, and its composition calculated by the expression on page 5.



#### IV. Summary.

1. Indirect methods for calculating bromides in the presence of chlorides are accurate only when the chloride concentration is low.
2. Slow precipitation of silver halides from ammonium hydroxide and from alcoholic solutions give unsatisfactory results in the presence of excess chlorides.
3. Low results for bromine are due to the solubility of silver bromide in alkaline halides.
4. Empirical corrections for low results are not feasible, since the solubility of silver bromide varies with its state of subdivision.
5. In selective oxidation processes the halogens are distilled into an absorption medium; sodium sulfite was studied as a reducing agent for this medium and proved troublesome by reducing the silver nitrate at high temperatures.
6. Hydrogen peroxide was found very satisfactory as an oxidizing agent for liberating the bromine, and as a reducing agent for reconvertng it to the bromide form.
7. An excess of oxidizing agent is desirable in the liberation of the bromine from the halide solution.
8. There is always a simultaneous liberation of chlorine along with the bromine in the oxidation of solutions of bromides and chlorides, particularly if the latter are present in quantity.
9. The simultaneous liberation of bromine and chlorine





is explained from thermodynamic considerations, which indicate that there is no oxidizing agent that will effect a satisfactory selective oxidation of bromine in the presence of chlorides in excess.

10. A new procedure of estimating bromine in the presence of chlorides is suggested.



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